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(19)

(54) ASSEMBLY OF A POROUS MEMBRANE ON A SUPPORT, AND THE PREPARATION THEREOF

(71) We, MICHELIN & CIE (COMPAGNIE GENERALE DES ETABLISSEMENTS MICHELIN), a French body corporate, of 4 Rue du Terrail, Clermont Ferrand, Puy-de-Dome, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

This invention relates to an assembly comprising at least one support secured to at least one membrane and to its preparation.

Such as an assembly is useful in cases where the support and the membrane assembled are used in a chemical and/or electrochemical apparatus particularly when the support, of which at least a portion of the surface conducts electrons, is intended to release electrons or collect electrons in a compartment of an electrochemical apparatus, the support being then usually known as an "electron collector". It will be apparent that these applications are not intended to be limitative, and that the support and the membrane assembled together can be used in apparatus other than chemical and/or electrochemical apparatus, for example in filters.

It is known to secure a support to a membrane by means of an adhesive material, which material may be for example thermoplastic, thermosetting or an elastomer. When it is desired to prepare an assembly with a porous membrane without losing the porosity of the membrane, this method then allows only imperfect adhesion between the contacting surfaces of the support and the membrane. In practice a partial or total dissociation of the assembly occurs. Besides the poor mechanical behaviour of the assembly due to this dissociation there are additional disadvantages. Thus, for example, in chemical and/or electrochemical apparatus using the assembly, there may be an accumulation of gas bubbles in the spaces formed because of the dissociation between the support and the membrane, so that there is defective operation of the portion of the apparatus situated near these bubbles, and this portion may be more particularly an electrode. Furthermore if the apparatus using the assembly comprises a fluid, more particularly a liquid in which particles are situated, the fluid and the particles being in movement, particles may penetrate into the spaces caused by the dissociation when the support is perforated, the dimensions of the openings in the support being larger than the mean diameter of the particles, which produces heterogeneity in the flow of the fluid and the particles, which heterogeneity is harmful to the operation of the apparatus and may lead to blocking of the apparatus.

French Patent Specification No. 821 466 discloses an electrode for an electrical accumulator which comprises an active material in electric contact with a light support which is made of a conductive material which can be attacked by the electrolyte. In order to avoid this support being attacked by the electrolyte and to reduce the weight of the electrode, there is interposed between the support and the active material a material which cannot be attacked by the electrolyte, for example, an insulating material, ducts being provided to extend through this material. All the ducts of the incorrodible material are filled with a metal by means of electrolysis so as to make the electrode impervious, that is to say to avoid contact between the electrolyte and the support, likewise to ensure the electrical connection between the support and the

active material. The method disclosed in this Patent eliminates the porosity of the insulating material, whereas such porosity is necessary in order to allow the migration of a fluid, for example an electrolyte, through the assembly, if such migration is desired.

It is an object of the present invention to obviate these disadvantages.

According to the invention there is provided a method of assembling at least one support, at least a portion of the surface of which conducts electrons, with at least one electrically insulating membrane which comprises pores having an average pore diameter which is substantially smaller than the thickness of the membrane at least some of the pores being open and having a sinuous structure, in which the membrane is contacted with at least a portion of the surface of the support which conducts electrons and at least one metal is electrolytically deposited on at least a portion of the electron-conducting surface of the support such that the electrolytically deposited metal extends within the open pores of the membrane in a filamentary and/or branched configuration to secure the membrane to the support, the growth of the deposit being regulated so that the electrolytically deposited metal does not extend through the membrane to ensure that the face of the membrane opposite the support remains electrically insulating, the assembled membrane being porous due to the presence of open pores without deposit, and the assembled structure being suitable for use in an electrochemical device.

Also according to the invention there is provided an assembly suitable for use in an electrochemical device comprising at least one support, at least a portion of whose surface conducts electrons, and at least one electrically insulating membrane which comprises pores having an average pore diameter which is substantially less than the thickness of the membrane at least some of the pores being open and having a sinuous structure, in which the membrane is secured to at least a portion of the electron-conducting surface of the support by an electrolytic deposit of at least one metal which is adhered to at least a portion of the conductive surface of the support and extends within open pores of the membrane in a filamentary and/or branched configuration, the deposited metal not extending through the membrane so that the face of the membrane opposite the support is electrically insulating, the assembled membrane being porous due to the presence of open pores without deposit.

The invention will now be described with reference to the accompanying drawings, in which:

Figure 1 represents a section through an apparatus suitable for use in the method according to the invention;

Figure 2 represents a section through a portion of an assembly produced by the method according to the invention;

Figure 3 represents a plan view of a portion of an assembly produced by the method according to the invention in which the membrane has been broken away from the assembly;

Figure 4 represents a perspective view of a further apparatus suitable for use in the method according to the invention; and

Figures 5 and 6 each represent in section an electro-chemical current generator utilizing at least one assembly according to the present invention.

Figure 1 illustrates an electrolytic apparatus 1 for carrying out the method according to the invention. The apparatus 1 comprises a metal anode 2 immersed in an electrolyte 3 contained in a tank 4. The assembly 5 is also immersed in the electrolyte 3, this assembly 5 comprising a support 6 acting as a cathode, and a membrane 7. By way of example, the anode 2 is in the form of a dish the bottom 8 of which is flat and horizontal, the assembly 5 being arranged within this dish 2. The membrane 7 has a general orientation parallel to the bottom 8 and the support 6 is in the form of a grid produced for example with a fabric or an expanded metal, this grid 6 being arranged above the membrane 7. The assembly 5, the general shape of which is planar is fixed on its edges in a frame 9 which is electrically insulating and is impervious to the electrolyte.

The membrane 7 is electrically insulating and comprises pores of which at least some are open pores. The membrane 7 may be prepared elsewhere, more particularly in the form of a film, and applied by compression to the support 6. Alternatively the membrane 7 may be prepared directly on the support 6, for example from a solution of at least one organic polymer in a solvent or a mixture of solvents, this solution being more particularly dispersed in the form of fibres on the support 6 according to the British Patent Specification No. 1,527,560. The membrane thus obtained by dispersion forms what is conventionally known as a "non-woven" structure which may if necessary be subjected to compression, on contact with the support, after evaporation of the solvent by drying.

The electrolyte 3 contains a solution of salt of a metal which it is desired to deposit by electrolysis to effect the assembly of the support 6 with the membrane 7.

Exemplary operating conditions are as follows:

support 6 and anode 2 are made from nickel;

membrane 7 comprises polyvinyl chloride;

aqueous electrolyte has a pH of 5 to 6 and contains about 40g/litre of Ni^{2+} ions (the nickel being for example introduced into the electrolyte in the form of nickel chloride) and 40g/litre of ammonium chloride;

electrolysis current between the anode 2 and the cathode 6 at a temperature of about 25°C: density of current 40 Ma per cm^2 of the face 10 of the membrane 7, this face 10 being directed towards the bottom 8 of the anode 2; current quantity 40 mAh per cm^2 of the face 10; use of a pulsed direct current, the ratio

$$\frac{Tp}{tn}$$

being approximately equal to 0.5 in which Tp being the time when current passes and Tn the time during which the current does not pass and, the frequency being approximately equal to 1 Hz.

It will be noted that at the end of depositing the adhesion between the support 6 and the membrane 7 constituting the final assembly 5 is considerably improved relatively to the initial adhesion of these components in the initial assembly 5. A possible explanation of the effect will be described with reference to Figure 2 which represents a portion of the assembly 5. In Figure 2 two open pores of the membrane 7 are illustrated; the pore 15 starting from the face 10 of the membrane 7 and ending at the portion 16 of the surface of the support 6 in contact with the membrane 7, and the pore 17 starting from the face 10 and ending at the portion 18 of the face 100 of the membrane 7 opposite from the face 10, this portion 18 being in contact with the electrolyte 3. Owing to the presence of the membrane 7 and the insulating frame 9, the electrical field lines, represented by the arrows E1, are to traverse the membrane 7 to arrive at the support 6 from the anode 2.

Since the membrane 7 is not electron-conducting, the electrical field follows the open pores, this electrical field being represented diagrammatically by broken lines E15 and E17 situated respectively in the pores 15 and 17. The field lines E15 terminating at the surface portion 16 of the support allow a deposit of nickel to be produced on this portion 16. During electrolysis, this deposit increases gradually in the pore 15 in the direction of the face 10 opposite from the support 6. Thus a filamentary deposit 19 is obtained in at least some of the open pores similar to the pore 15 connecting the face 10 of the membrane 7 to the support 6, these open pores optionally communicating with one another. These filamentary deposits 19, which may comprise branched portions because of communication between the open pores, permit attachment of the support 6 to the membrane 7 and consequently good mechanical strength for the assembly 5. This attachment is particularly effective since the open pores 15 have a sinuous structure and more particularly when the deposits 19 are branched.

The field lines E17 arriving at the portion 18 in contact with the electrolyte 3 diverge in the electrolyte 3, giving a fan formation of field lines E6 terminating at a considerable zone (not given a reference numeral) of the surface of the support 6 in contact with the electrolyte 3, thus bringing about a deposit of nickel which is substantially uniform and not very thick on this zone. Figure 3 shows a portion of the support 6 after electrolysis and with the membrane 7 initially assembled with the support 6 according to the invention removed, this membrane having being prepared as a film elsewhere and applied to the support prior to electrolysis. It will be noted that there are arborescent deposits 22 at the side where the membrane was situated on the nodes or junctions 23 of the grid 6 which is made with an expanded metal or a fabric, these arborescent deposits 22 being formed by the joining together of filamentary deposits 19. The branches 24 of the grid 6 do not have such arborescent deposits because during electrolysis the junctions 23 were in contact with the membrane whilst the branches 24 had non-existent or poor contact with the membrane. The number of junctions 23 should be sufficient to provide good mechanical strength for the assembly 5. Therefore, it is important that the support 6 should have sufficient contact zones with the membrane during electrolysis, hence the advantage in applying the membrane to the support by compression when the membrane is prepared elsewhere. When the membrane is prepared directly on the support 6, more particularly according to the method described in British Patent Specification No. 1,527,560 a good contact is obtained between the support 6 and the membrane 7 in such a manner that compression is not usually necessary. The pressure used for the possible compression operation may vary within very wide limits, for example from 1 kg/cm^2 to several tens of kg/cm^2 and this pressure may be applied before and/or even advantageously during electrolysis.

The face 10 should remain insulating, and so the growth of deposits 19 is regulated so that they do not extend through the membrane 7.

It should also be noted that it is possible if desired to obstruct all or some of the open pores of the membrane 7 after the deposits 19 have been produced. This obstruction may be carried out for example by filling these pores with a material or compressing the face 10 of the membrane 7, which face is preferably then raised to a temperature permitting the melting or softening of the material constituting this face.

The structure of the apparatus 1 makes it possible to obtain electrical field lines E1 which are substantially parallel between the anode 2 and the cathode 6. This parallel orientation of field lines is preferable since it makes it possible to have substantially uniform distribution of field lines over the face 10 of the membrane 7 and consequently optimum distribution of deposits 19.

Attachment between the filamentary deposit 19 and the support 6 is usually achieved under optimum conditions when the metal of this deposit 19 is identical with the metal constituting the support 6, but this operating condition is not vital as it is possible to use different metals for the deposit 19 and the support 6. The metal used for producing the deposit 19 is then chosen preferably in accordance with the nature of the support 6 in order to avoid the formation of galvanic couplings when the assembly 5 is used.

In addition to nickel, the metals which can be used for making the deposit 19 can be numerous, for instance, copper, iron, silver, gold, platinum. It will be apparent also that it is possible to deposit several metals during the same electrolysis operation and that the support 6 can be made with a metal alloy comprising possibly the same metal as that of the deposit or even with any other non-metallic substance conducting electrons, for example carbides or nitrides. It is not essential that the entire mass of the support 6 should conduct electrons, and it is possible to use supports 6 made of a material which does not conduct electrons, for example glass, ceramic, a macromolecular material, this material being coated wholly or partially with a material which is electron-conducting, the deposit 19 being deposited on the conductive material in this case.

The best attachments between the membrane 7 and the support 6 are obtained by effecting electrolysis with a pulsed current, as described above. This is probably due to the fact that when the membrane is thick or when its open pores are very fine, the use of a nonpulsed direct current brings about an ion impoverishment of the metal deposited in the open pores, which promotes the accumulation in these pores of products coming from the parasitic electrolysis reaction of the solvent. The formation of the deposit 19 is then disturbed.

In Figures 1 to 3 the support 6 is in the form of a grid, but it will be apparent that any other form of support could be used, for example a sheet which may or may not be provided with perforations.

It will be also be clear that the support 6 and the membrane 7 are not necessarily planar. It is possible to envisage other shapes, for example tubular shapes, in which case the anode 2 is preferably also tubular in shape, as in the apparatus 30 shown in Figure 4. In this apparatus 30, the anode 32 is in the form of a cylinder of revolution on the axis XX′, this axis XX′ being for example vertical. Within this cylinder 32 there is arranged the assembly 35 comprising the support 36 and the membrane 37 in contact with one another, this support 36 and this membrane 37 being in the form of cylinders of revolution with the axis XX′. The membrane 37 is arranged between the anode 32 and the electron-conducting support 36 which is used as a cathode. The assembly 35 and the anode 32 are immersed in an electrolyte (not shown) contained in a tank (not shown). The upper and lower edges of the assembly 35 are preferably fixed in insulating frames (not shown) in a way similar to the frame 9 in Figure 1 so that the electrical field lines shown diagrammatically by the arrows E4 between the anodes 32 and the membrane 37 are substantially radial, that is to say directed towards the axis XX′ and perpendicular to this axis. The field lines are then distributed in uniform manner on the surface 38 of the membrane 37, this surface 38 being opposite from the support 36.

After electrolysis there is obtained an assembly 35 comprising the cylinders 36 and 37 attached to one another by means of the deposits 19 previously described, the supporting cylinder 36 being situated within the assembly 35. It is possible to use this assembly 35 as it is or to deform or unwind it after having cut it, so as to obtain a flat assembly similar to the assembly 5. It will be apparent that by arranging the support 36 and the membrane 37 outside the anode 32, the membrane 37 being arranged between the anode 32 and the support 36, these components being again cylinders of revolution having the same axis, there is thus obtained an assembly comprising the cylinders 36 and 37 and the deposits 19, the support 36 being situated outside the membrane 37.

It is also possible to use more than one anode in electrolysis apparatus making it possible to use the method according to the invention, and that several assemblies according to the invention can be produced simultaneously in the same apparatus. It will be apparent also that the assemblies according to the invention may if necessary comprise several supports and/or several membranes each.

Figure 5 represents an apparatus 40 using at least one assembly 5 shown in Figure 1. This apparatus 40 is an electro-chemical electrical current generator comprising a cell 41 which comprises an anode compartment 42 and a cathode compartment 43. This cathode compartment 43 comprises a cathode 44 the general shape of which is substantially planar which is for example an oxygen or air diffusion electrode, the inflow and outflow of gas into and from the cathode compartment 43 being shown diagrammatically by the arrows F4 and F5 respectively.

The cathodic collector 45, intended to deliver into the cathode 44 the electrons necessary for the reduction of the oxygen, active cathodic material, is connected to the positive terminal P of the generator.

The cell 41 uses an assembly identical to the assembly 5 arranged in such a manner that the membrane 7 is against the cathode 44, this assembled membrane being porous because of the presence of open pores not having a deposit 19. The support 6 in the form of a grid for the assembly 5 is arranged at the side opposite from the cathode 44 relative to the membrane 7. This grid 6 is used as an anodic collector and it is connected to the negative terminal N of the generator 40. The deposits 19 of the assembly 5 are such that they do not extend entirely through the membrane 7, so as to prevent any short-circuit with the electron-conducting portions of the cathode 44, these deposits 19 extending for example between 10% and 90% and preferably about 50% through the thickness "e" of the membrane 7, this thickness "e", greater preferably than 50 microns, ranging for example from 0.1 to 1.5 mm.

The main features of the assembly 5 are for example as follows:

a) membrane 7: PVC membrane commercially available from the Amerace Company, this is a hydrophilic membrane with open pores being made essentially or polyvinyl chloride and silicon dioxide; thickness about 0.6 mm, mean diameter of pores less than 5 microns, for example about 0.1 micron;

b) grid 6 made from a sheet of expanded metal, more particularly a copper sheet, comprising about 60 junctions 23 per cm^2; each main face 160, 161 of the grid 6 (Figures 1 and 3) comprises about 20% to 50%, for example about 30%, of free surface corresponding to the openings 600 of the grid 6 (Figures 3 and 5); 50% to 80% of each face 160, 161 therefore correspond to a metal surface;

c) the membrane 7 is applied to the grid 6, so that the main faces 160 of the grid 6 and 100 of the membrane 7 are in contact with one another during electrolysis; the deposits 19 are made of copper; after electrolysis, about 20% to 50%, for example about 30% of the metal surface of the face 160 of the grid 6 in contact with the membrane 7 is covered with arborescent deposits 22 these deposits covering only the portions 220 of the surface of the junctions 23 of the grid 6, on the face 160 of the grid 6 in contact with the membrane 7 (Figure 3), the branches 24 of the grid not having such deposits; the fraction of the surface of the grid 6 covered by the deposits 22 therefore corresponds to the portions 220 which are determined macroscopically, that is to say they comprehend both the effective sections of the deposits 19 and the surface of the support 6 situated between the deposits 19 which are situated near to one another; assuming that the distribution of open pores 15, 17 on the face 100 of the membrane 7 is substantially uniform, these percentages correspond substantially to the percentages of open pores 15 opening onto the support 6 which comprises deposits 19, only a limited number of such open pores 15 comprising deposits 19; therefore the electrolytic deposit covers at the most only about 40% of the mutually facing faces 160 and 100 of the support 6 and the membrane 7, since the portions of the face 100 of the membrane opposite the openings 600 do not comprise a deposit 19; this distribution of arborescent deposits 22 is obtained probably because of an effect known as a "point" effect during electrolysis, this effect causing a preferential deposit on the protuberances of the expanded metal 6 which are situated essentially at the junctions 23;

d) absorption of aqueous solution of 8N potassium hydroxide (8 moles of potassium hydroxide per litre) in the membrane 7, measurements being effected at ambient temperature, that is to say about 20°C, after impregnation for 24 hours: the ratio

$$R = \frac{P_1 - P_0}{P_0} \times 100$$

is equal to about 170 before the assembly 5 is made and 160 approximately after the assembly has been produced, P_1 and P_0 representing respectively the weight of the membrane 7 after and before absorption of

the potassium hydroxide solution; this ratio, which therefore varies very little when the assembly 5 is produced, gives a faithful image of the perviousness of the membrane 7 to this solution, this perviousness being obtained by means of the open pores 15, 17 which do not have a deposit 19;

e) electrical measurements taken on the membrane 7; the transverse resistance per unit of surface of this membrane is substantially the same before and after production of the assembly 5, and is about $0.16\Omega cm^2$, this measurement being effected by ionic conduction with a pulsed current in an aqueous solution of 8N potassium hydroxide at approximately 20°C after impregnation for 24 hours; this resistance, for a thickness of the membrane 7 equal to 0.6 mm corresponds to a specific resistivity of approximately $2.66\Omega cm$, whilst the aqueous potassium hydroxide 8N has a specific resistivity of about $1.80\Omega cm$ at 20°C.

The cathode 44 may if necessary comprise a porous membrane 46 in contact with the membrane 7 of the assembly 5, so as to reduce further risk of short circuits between the anodic collector 6 and the cathode 44, this membrane 46 optionally being prepared for example directly on the body of the cathode 44 according to British Patent Specification No. 1,527,560, from a solution of at least one organic polymer in a solvent or a mixture of solvents. The contact between the membrane 7 and the electrode 44 with or without membrane 46 can be effected by compression and/or utilizing a binding agent.

The anodic compartment 42 is filled with an electrolyte 47, for example, an alkaline electrolyte, more particularly aqueous potassium hydroxide, e.g. a solution of 4 to 12N potassium hydroxide containing 4 to 12 moles of potassium hydroxide per litre.

This electrolyte 47 contains particles 48 including an active anodic metal, these particles 48 being for example particles of zinc which oxidise in the anodic compartment 42, losing electrons collected by the anodic collector 6. According to British Patent Application No. 32994/77 (Serial No. 1,587,166), the particles 48 can form for example a sedimentation bed 49 adjacent the anodic collector 6 which is then arranged at the lower portion of the interior of the anodic compartment 42.

The movements of the particles 48 in this bed 49, carried along by the electrolyte in the mean direction indicated diagrammatically by the arrow F6, in this case promotes diffusion in the electrolyte of the reaction products.

The supply apparatus, indicated diagrammatically by the arrow F7, introduces the electrolyte 47 and the particles 48 into the anodic compartment 42. This device F7 may be for example one of the supply devices described in British Patent Application No. 32995/77 (Serial No. 1,555,863) which make it possible to form a divergence of the flow lines. The device indicated diagrammatically by the arrow F8 allows the electrolyte 47 to be removed from the anode compartment 42 and the particles 48 which have not been entirely consumed during their passage in the compartment. The device F8 may be for example one of the removal devices described in British Patent Application No. 32995/77 (Serial No. 1,555,863), which make it possible to converge the flow lines. The device F8 is connected to the device F7 by a path 50 outside the cell 41, this line including the pump 51 allowing the circulation of the electrolyte 47 and the particles 48 in the anode compartment 42, in line 50 and in the devices F7 and F8, and the buffer tank 52 of the electrolyte 47 and particles 48. The device 53 ending at the line 50 regulates the percentage by weight of particles 48 in the electrolyte 47 constant if so desired. The porous membrane 7, impervious to the particles 48, and the porous membrane 46 if that is used, have a hydrophilic character, which facilitates the diffusion of the electrolyte 47 through these membranes and consequently, ion exchanges through the apertures 600 of the grid 6 between the electrolyte 47 and the cathode 44 whose body is made for example in a known manner substantially of nickel, activated carbon, silver and a fluorine polymer.

The concentration of zinc dissolved in the electrolyte is maintained below a limit beyond which the particles 48 would be rendered passive, such a limit being for example about 120 g/litre of electrolyte when the electrolyte 47 is 6N potassium hydroxide (6 moles of potassium hydroxide per litre).

During the operation of the generator, no separation is found between the grid 6 and the membrane 7, and consequently no accumulation of gas bubbles, and also no accumulation of particles 48 between the grid 6 and the membrane 7 when the mean diameter of the particles 48 is below the dimensions of the apertures 600 of the grid 6.

This result is surprising given that only a small portion of the face 100 of the membrane 7 is connected to the face 160 of the grid 6 by the arborescent deposits 22. The generator 40 can therefore operate continuously, without passivation of the particles 48 and without obstruction of the anode compartment 42, the cathode 44 operating in a substantially uniform manner owing to the satisfactory perviousness of the

membrane 7 to the electrolyte, in the assembly 5.

It should be noted that it is possible to envisage other constructional forms of the assembly 5, more particularly an arrangement such that the arborescent deposits 22 cover substantially all the surface of the grid 6 in contact with the membrane 7.

The cell 41 may have a symmetrical structure. In that case it comprises another cathode compartment 54, for example identical with the cathode compartment 43 and arranged parallel to this compartment 43 and above, the references F4, F5, 44, 45, 46 relating to the cathode compartment 54 having the same meanings as in the case of the cathode compartment 43. Another assembly 55 identical for example to the assembly 5, is then arranged in such a manner that its membrane 7 is arranged against the cathode 44 of the cathode compartment 54, if appropriate by means of the membrane 46 of this compartment 54, the grid 6 of this assembly 55 being arranged at the side opposite from this cathode 44 relatively to the said membrane 7, this grid 6 thus acting as an upper anodic collector.

The electrolyte 47 and the particles 48 then flow between the two anodic grids 6. This arrangement makes it possible substantially to double the power of the cell 41, the other operating conditions remaining identical.

Figure 6 represents an electrochemical generator 60 similar to the generator 40 but using the cylindrical assembly 35 shown in Figure 4. This generator 60 comprises a cell 61 the general shape of which is cylindrical, at the centre of which the assembly 35 is situated.

The interior of the assembly 35 comprises the anode compartment 62 where the electrolyte 47 and the particles 48 flow, the support 36 being in the form of a grid conducting the electrons, situated at the region of the electrolyte 47 and the particles 48. A tubular cathode 64 with the same axis XX' as that of the assembly 35, this axis XX' being situated in the plane of Figure 6, is applied externally of the assembly 35 and around the porous membrane 37, this cathode 64 optionally comprising a porous membrane 66 in contact with the membrane 37. The inflow and outflow of gas into and from the cathode compartment 63 where there is situated the cathode 64 with its collector 65, connected to the positive terminal P of the cell 61, are designated diagrammatically respectively by the arrows F4 and F5. The conduit 67 is used for introducing electrolyte 47 containing particles 48 into the anode compartment 62, the conduit 68 being used for removing the electrolyte 47 and the particles 48 which have not been entirely consumed during their passage in the anode compartment 62. The flow of electrolyte 47 and the particles 48 in the compartment 62 takes place in turbulent fashion so that the particles 48 are subjected to repeated contact with all the surface of the tubular grid 36, which acts as an anodic collector connected to the negative terminal N of the cell 61.

The generators 40 and 60 previously described comprise only one cell, but it is possible to envisage electro-chemical generators comprising a plurality of cells each using at least one assembly according to the present invention.

It will be apparent that in the electrochemical generators 40 and 60 described hereinbefore it is possible to use cathodes whose active material is not a gas, for example cathodes comprising at least one oxygen-containing compound, more particularly a metal oxide. It is also apparent that the generators may if necessary operate even if the membranes 7 and 37 are not applied against the corresponding cathodes 44 and 64, these membranes being where appropriate separated from the respective cathodes in that case by an electrolyte.

WHAT WE CLAIM IS:—

1. A method of assembling at least one support, at least a portion of the surface of which conducts electrons, with at least one electrically insulating membrane which comprises pores having an average pore diameter which is substantially smaller than the thickness of the membrane, at least some of the pores being open and having a sinuous structure, in which the membrane is contacted with at least a portion of the surface of the support which conducts electrons and at least one metal is electrolytically deposited on at least a portion of the electron-conducting surface of the support such that the electrolytically deposited metal extends within open pores of the membrane in a filamentary and/or branched configuration to secure the membrane to the support, the growth of the deposit being regulated so that the electrolytically deposited metal does not extend through the membrane to ensure that the face of the membrane opposite the support remains electrically insulating the assembled membrane being porous due to the presence of open pores without deposit and the assembled structure being suitable for use in an electrochemical device.

2. A method as claimed in Claim 1 in which the support is used as a cathode during the electrolytic deposition of the metal and at least one anode is arranged so that the electrical field lines connecting the

anode and the cathode pass through the membrane.

3. A method as claimed in Claim 2 in which the electrical field lines from the anode are distributed in a substantially uniform manner over the surface of the membrane.

4. A method as claimed in any preceding claim in which the membrane is applied by compression to the support before and/or during electrolysis.

5. A method as claimed in any preceding claim in which the membrane is prepared from a solution of at least one organic polymer in a solvent or a mixture of solvents, the solution being dispersed in the form of fibres on the support.

6. A method as claimed in any preceding claim in which the electrolytic deposition is effected utilizing a pulsed direct current.

7. A method as claimed in Claim 6 in which the ratio

$$\frac{Tp}{Tn}$$

is about 0.5 in which Tp is the current passage time and Tn the time during which the current does not pass, the frequency being approximately equal to 1 Hz.

8. A method as claimed in any preceding Claim in which the electron-conducting surface of the support comprises metal or metal alloy.

9. A method as claimed in Claim 8, in which the deposited metal is the same as the metal comprising the electron-conducting surface of the support, or a metal of the metal alloy comprising the electron-conducting surface of the support.

10. A method as claimed in any preceding claim in which the electrolytically deposited metal covers only a portion of the surface of the support in contact with the membrane.

11. A method as claimed in any preceding claim in which the support is apertured.

12. A method as claimed in Claim 11 in which the main face of the support in contact with the membrane has about 20 to 50% free surface.

13. A method of assembling at least one support with at least one membrane substantially as herein described with reference to any one of Figures 1 to 4 of the accompanying drawings.

14. A support and membrane assembly prepared by a method as claimed in any preceding claim.

15. An assembly suitable for use in an electrochemical device comprising at least one support, at least a portion of whose surface conducts electrons, and at least one electrically insulating membrane which comprises pores having an average pore diameter which is substantially less than the thickness of the membrane, at least some of the pores being open and having a sinuous structure, in which the membrane is secured to at least a portion of the electron-conducting surface of the support by an electrolytic deposit of at least one metal which is adhered to at least a portion of the conductive surface of the support and extends within open pores of the membrane in a filamentary and/or branched configuration, the deposited metal not extending through the membrane so that the face of the membrane opposite the support is electrically insulating, the assembled membrane being porous due to the presence of open pores without deposit.

16. An assembly as claimed in Claim 15, in which the membrane comprises fibres forming a "non-woven" structure.

17. An assembly as claimed in Claim 15 or Claim 16, in which the electron-conducting surface of the support comprises a metal or an alloy.

18. An assembly as claimed in Claim 17, in which the electrically deposited metal is the same as the metal constituting the electron-conducting surface of the support, or a metal of the alloy comprising the electron-conducting surface of the support.

19. An assembly as claimed in any one of Claims 15 to 18 in which the electrolytically deposited metal is nickel, copper, iron, silver, gold, platinum.

20. An assembly as claimed in any one of Claims 15 to 19 in which the deposit is approximately 50% of the thickness of the membrane.

21. An assembly as claimed in any one of Claims 15 to 20 in which the membrane is hydrophilic.

22. An assembly as claimed in any one of Claims 15 to 21 in which the support is apertured.

23. An assembly as claimed in any one of Claims 15 to 22 in which the electrolytically deposited metal covers only a portion of the surface of the support in contact with the membrane.

24. An assembly as claimed in Claim 23 in which the deposit covers only 20 to 50% of the surface of the support in contact with the membrane.

25. An assembly as claimed in any one of Claims 22 to 24 in which the main face of the support in contact with the membrane has about 20 to 50% free surface.

26. An assembly as claimed in any one of Claims 23 to 25, in which the support comprises protuberances.

27. An assembly comprising at least one support secured to at least one membrane substantially as herein described with reference to any one of the accompanying drawings.

28. Apparatus comprising an assembly as claimed in any one of Claims 14 to 27.

29. An electrochemical generator comprising apparatus as claimed in Claim 28.

30. An electrochemical generator as claimed in Claim 29 comprising at least one anode compartment and at least one cathode compartment, the anode compartment containing an electrolyte in which there are situated particles constituted at least partly by an active anodic metal, the apertures support arranged at the electrolyte side acting as an anodic collector, the membrane being arranged in the region of the or a cathodic compartment.

31. An electrochemical generator as claimed in Claim 30 in which the active anodic metal is zinc, the electrolyte is an alkaline electrolyte and the active cathodic material is oxygen, or an oxygen compound.

32. An electrochemical generator substantially as herein described with reference to Figure 5 or Figure 6 of the accompanying drawings.

For the Applicants,
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fig.1

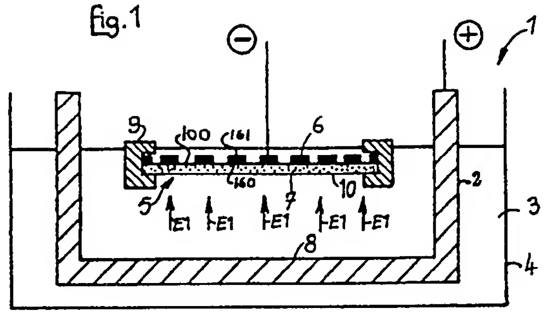

1
9
100
161
6
160
7
10
5
E1
E1
E1
E1
E1
2
3
8
4

fig.2

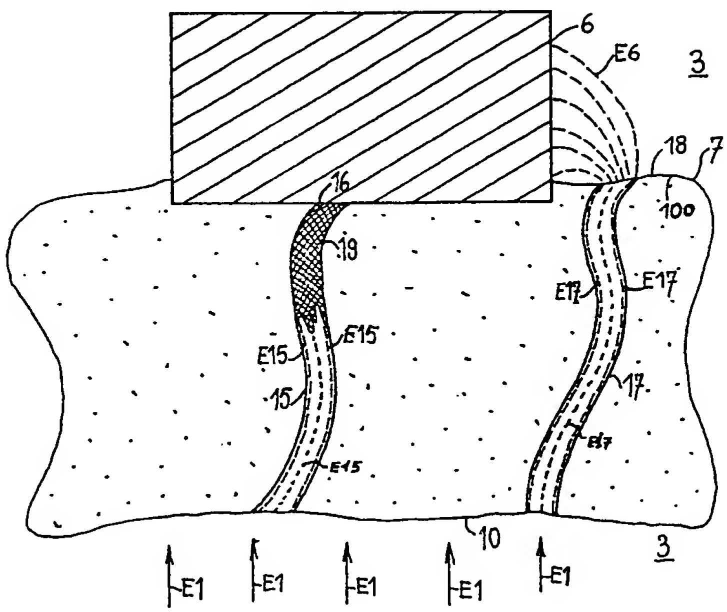

6
E6
3
18
7
100
16
19
E17
E17
E15
E15
15
17
E17
E15
10
3
E1
E1
E1
E1
E1

Fig. 3

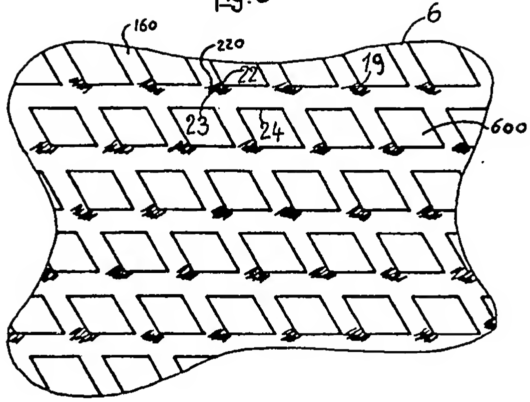
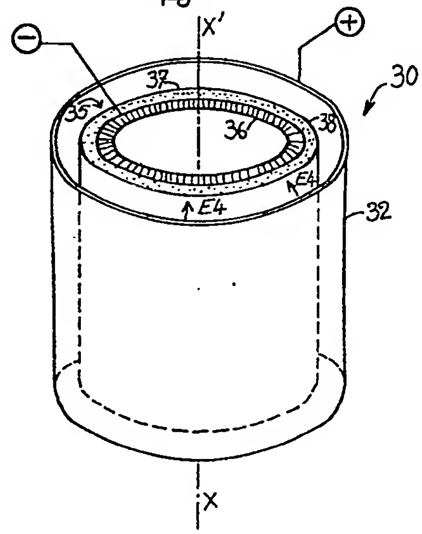


Fig. 4



1692981 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 3

fig.5

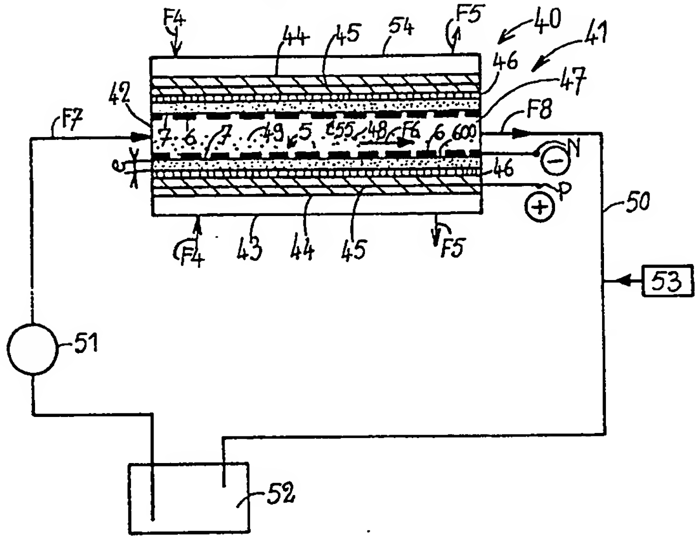


fig.6